High Yield Monoglycerides Preparation from Glycidol and Carboxylic Acids

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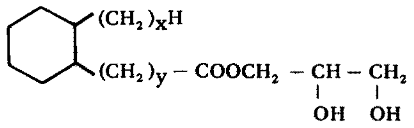
ABSTRACT

In the present work we examined the reaction conditions that maximize the yield in monoglycerides (>90%) of 2,3-epoxy-1-propanol (glycidol) reaction with carboxylic acids. Mono- and dicarboxylic acids of different chemical structures are used in this study. It was found that the reaction rate depends upon the temperature, the molar excess of glycidol, the structure and the length of the carbon chain of carboxylic acids. Further, the reaction is positively affected by the use of tetraethylammoniumiodide as catalyst. A technique is proposed to improve the glycidol method which appears to be very efficient for the continuous production of monoglycerides in high yields.

INTRODUCTION

In addition to being used as food additives, monoglycerides also are employed as polymer additives. Therefore, the need for more efficient methods of monoglyceride preparation is obvious. Their consumption in Europe exceeds 20,000 tons per annum. Monoglycerides of a purity lower than 90% are derived either from the catalytic transesterification of glycerol with triacylglycerols (1,2) or from the direct esterification of free fatty acids with glycerol (3,4). For the industrial preparation of monoglycerides of a purity higher than 90%, synthesized monoglycerides undergo molecular distillation, a process which increases their manufacturing cost.

The present study was undertaken in an attempt to prepare monoglycerides in good yield and high purity. We found that these aims are fulfilled by using glycidol (a toxic compound hazardous to health, especially when swallowed or in contact with the skin) as the esterification agent. In addition to more common acids, monoglycerides in high purity are obtained even in cases such as the hydrogenated cyclic fatty acids (HCFAM) (5) in which the standard methods of esterification are not successful.



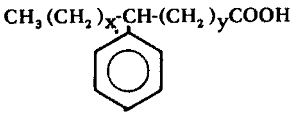
x + y = 11

The main advantage of the new method is that it does not require any molecular distillation to obtain monoglycerides of high purity.

EXPERIMENTAL

Principal Starting Materials

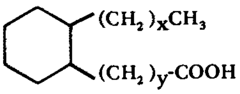
Glycidol (2,3-epoxy-1-propanol) was purchased from Research Org. Inorg. Chem. Corp., Sun Valley, California. Hydrogenated abietic acid was prepared from abietic acid (purity >97%, Fluka) through hydrogenation with 10% Pd/C (5% Pd)/10h at 180-200 C and 25 atm. pressure. GC/MS analysis: ca 45% dihydroabietic acid, 30% tetrahydroabietic acid and 20% dehydroabietic acid. Acid value (AV) 203 (theor. 214). Hydrogenated cyclohexylundecanoic acid was prepared from phenylundecanoic acid of structure:



x + y = 8

through hydrogenation with 0.25% PtO_2, in acetic acid, 6 hr at 180-200 C and 140 atm. pressure. Bp = 175-178 C/0,3 mm Hg; AV = 209 (theor. 209); UV-spectrum: no absorption in the aromatic range.

Hexahydrophthalic acid-mono-n-octylester was prepared from hexahydrophthalic acid anhydrate (ex Merck) and Na-n-octylalkolate (S. Zlatanos and A. Sagredos, publication in preparation). AV = 197 (theor. 197); mp = 9.5-10.5 C (Hexan); GC of Me-ester < 99.0% purity. Hydrogenated cyclic fatty acids monoglycerides (HCFAM) were prepared from hydrogenated cyclic fatty acids (HCFA) and glycidol. Hydrogenated fatty acids were obtained from cyclic fatty acids resulting from cyclization of linseed oil (7). Hydrogenation conditions: 0.25% PtO_2, 20 hr, 180-200 C, 160 atm. in acetic acid. GC/MS analysis of the Me-ester showed the following structure (8):



x + y = 10

Phthalic acid mono-n-octylester was prepared (S. Zlatanos and A. Sagredos, publication in preparation) from Na-n-octanolate (Merck) and phthalic acid anhydride (Merck). AV = 201.5 (theor. 201.5); mp = 24-25 C (Hexan) GC of Me^+-ester showed < 99% purity. The rest of the fatty acids used in this work were purchased from Merck.

Thin Layer Chromatography (TLC)

TLC plates were prepared from silica gel (Merck) containing boric acid (11.48 g H_3BO_3/60 ml H_2O). The thickness of the plates was 0.25 mm. The samples were dissolved in chloroform, and the developing mixture was chloroform, acetone and acetic acid (94:4:0.5). The plates were sprayed with a 10% solution of phosphomolybdic acid in ethanol.

Monoglycerides

For the formation of monoglycerides the carboxylic acid and the tetraethylammoniumiodide (catalyst) are placed in a round bottom flask. At a specified temperature (Table I) glycidol is added and the content of the flask is well stirred. The acidity of the reaction mixture is determined every 5 min, and the concentration of di- and triglycerides are traced by thin layer chromatography (TLC).

The temperature remains constant during the reaction. The reaction is terminated before the acid value approaches zero. The content of the flask is then diluted with water, and the reaction product is extracted with diethylether.

Continuous Formation of Caprylic Acid Monoglycerides

A mixture of 28.8 g (0.2 mole) of caprylic acid, 22.2 g (0.3 mole) of glycidol and 0.28 g of tetraethylammoniumiodide is fed continuously (1 drop per 6 sec) to a stainless steel reactor coil of 2 mm inner diameter and 2 m length, which is placed in a glycerol bath at 120 C. The mean residence time of the reaction mixture is about 60 min.

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TABLE I

Optimum Conditions for the Esterification Reactions of Various Carboxylic Acids and Mono-ester Dicarboxylic Acids with Glycidol

Carboxylic acid	Acid:glycidol molecular ratio	% Catalyst $(C_2H_5)_4$ NI calculated on the weight of acid	Time min	Temperature °C	Acid value	% Monoglycerides[a]		% Glycerol	Thin layer chromatography[b]
						α-	β-		
Caprylic	1:6	–	45	160	1.3	96	–	1.04	+
Caprylic	1:1.5	1	50	110	3.1	84	6	1.2	++
2-Ethylcaproic	1:6	–	40	160	1.2	97	–	1.02	+
Lauric	1:6	–	60	160	1.7	85	7	1.9	++
Stearic	1:1.5	1	35	100	4.2	88	–	2.1	+
Oleic	1:1.5	1	40	110	3.4	75	8	2.1	++
HCFA	1:6	–	70	160	1.9	96	–	1.9	+
HCFA	1:1.5	1	42	100	2.2	87	5	2.3	++
Cyclohexylundecanoic	1:6	–	20	160	5.2	90	3	2.2	+
Cyclohexylundecanoic	1:6	–	40	130	2.1	93	2	1.9	+
Mono-n-octyl-ester of hexahydrophthalic	1:6	–	20	160	1.2	98	–	1.1	+
Mono-n-octyl-ester of phthalic	1:1.5	1	30	100	3.9	84	6	1.9	++
Terephthalic	1:12	–	30	130	3.5	51	19	3.1	+++
Terephthalic	1:3	0.5	60	110-130	1.2	54	22	3.0	+++
Abietic	1:3	–	30	130	0.3	98	–	1.05	+
Abietic	1:1.5	–	70	130	1.1	89	6	1.8	+
Abietic	1:1.5	0.3	26	130	2.3	85	5	1.9	+
Hydrogenated abietic	1:3	–	25	130	0.4	98	–	1.06	+

[a] Product composition, purity higher than 97%.

[b] +, Free from di- and triglyceride; ++, traces di- and triglycerides; +++, visible impurities of terephthalic acid diglyceride.

TABLE II

Mean Rates of Esterification of Caprylic Acid in a Stainless Steel Coil Reactor

Time min	Acid value (mg KOH/g)	TLC (silica gel impregnated with H_3BO_3)
0	216	
20	54.2	Mono- with traces of di- and triglycerides
30	27.6	Mono- with traces of di- and triglycerides
40	11.8	Mono- with traces of di- and triglycerides
45	6.1	Mono- with traces of di- and triglycerides
50	2.3	Mono- with di- and triglycerides
55	1.1	Mono- with di- and triglycerides
≥ 60	<1	Mono- with di- and triglycerides

TABLE III

Mean Rates of Esterification of Caprylic Acid in a Pyrex Coil Reactor

Time min	Acid value (mg KOH/g)	TLC (silica gel impregnated with H_3BO_3)
0	216	
20	54.8	Mono- with traces of di- and triglycerides
30	31.9	Mono- with traces of di- and triglycerides
40	22.3	Mono- with di- and triglycerides
45	12.6	Mono- with di- and triglycerides
50	10.1	Mono- with di- and triglycerides
≥ 80	<1	Mono- with di- and triglycerides

The acid value and the TLC composition of the reaction product from the coil reactor during its transient operation from a set of 10 experiments under the conditions described are shown in Table II.

The experiment was repeated using a glass coil reactor of similar dimensions instead of the stainless steel reactor coil. For identical experimental conditions the acid value and the TLC composition of the reaction products, during their transient operations, are shown in Table III.

A comparison of the values presented in the two tables indicates two important points: (i) The reaction is faster in the stainless steel coil reactor than in the glass one. (ii) The concentration of di- and triglycerides is lower in the stainless steel coil reactor than in the glass coil reactor.

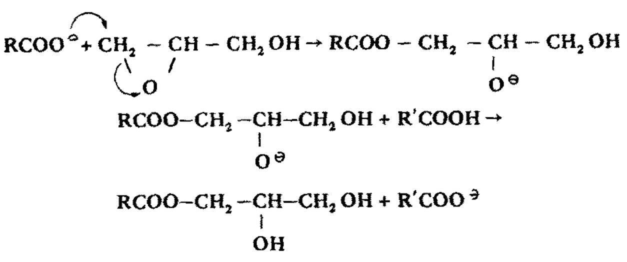
A series of experiments with different geometries were carried out subsequently and the results, similar to those presented in Tables II and III, were consistent with the above two points. This difference should be attributed to the alkalinity of the glass coil.

Determination of Monoglycerides and Free Glycerol

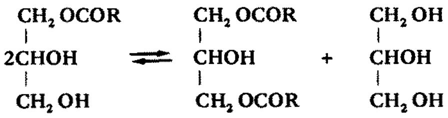
The final concentration of a-monoglycerides and the free glycerol are determined according to Kruty's method (9). The final β-monoglyceride concentration is determined by Brokaw's method (10).

RESULTS AND DISCUSSION

From Table I it can be seen that the main products of the glycidol esterification reaction with various acids are α-monoglycerides. The esterification reaction follows an S_N2 mechanism (6).



A TLC analysis of the reaction products showed that there are only traces of di- and triglycerides. It was found that transesterification will take place at the end of the glycidol esterification reaction when the total amount of acid has reacted. Apparently, the diglycerides result from a slow metathesis reaction and their concentration is increased with time.

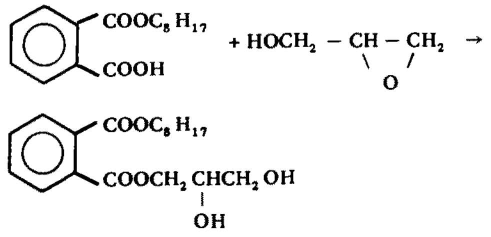


$$\begin{array}{c}\mathrm{CH_2OCOR}\\|\\\mathrm{2CHOH}\\|\\\mathrm{CH_2OH}\end{array} \rightleftharpoons \begin{array}{c}\mathrm{CH_2OCOR}\\|\\\mathrm{CHOH}\\|\\\mathrm{CH_2OCOR}\end{array} + \begin{array}{c}\mathrm{CH_2OH}\\|\\\mathrm{CHOH}\\|\\\mathrm{CH_2OH}\end{array}$$

The formation of diglycerides may be avoided by adding distilled water when the acid value of the mixture approaches zero. This method seems to be suitable for the selective production of α-monoglycerides of high purity with or without the presence of a catalyst. The results of this study show that caprylic acid reacts faster than lauric acid, but the reaction is slower than the mono-n-octylester of hexahydrophthalic acid. From the results of this investigation we can conclude that the tertiary aromatic carboxylic groups react faster than the primary aliphatic ones, and the branched aliphatic acids react faster than the non-branched.

The reaction of the abietic acid and 4,5-dihydroabietic acid is extremely fast either with or without the presence of catalyst, whenever glycidol is in excess. Finally, the activation energy of the esterification reaction was calculated from an Arrhenius plot and found equal to 27.5 kcal/mol. Tetraethylammoniumiodide (TEAI) was found to be very effecient as catalyst. The reaction proceeds quickly in the presence of TEAI catalyst, even at low temperatures and low glycidol concentrations.

Preliminary results obtained from the continuous process showed that the final product consisted mainly of monoglycerides and small amounts di- and triglycerides. This indicates that the continuous production of monoglycerides is feasible. The new method, apart from having a higher yield, also can be used for the formation of monoglycerides which hardly can be produced by other methods, e.g. the monoglycerides of mono-n-octylester of hexahydrophthalic acid and of mono-n-octylester of phthalic acid.



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[Received November 29, 1984]